

# The distribution of hydrogen, nitrogen, and chlorine radicals in the lower stratosphere: Implications for changes in O<sub>3</sub> due to emission of NO<sub>y</sub> from supersonic aircraft

R. J. Salawitch<sup>1</sup>, S. C. Wofsy<sup>1</sup>, P. O. Wennberg<sup>1</sup>, R. C. Cohen<sup>1</sup>, J. G. Anderson<sup>1</sup>, D. W. Fahey<sup>2</sup>, R. S. Gao<sup>2</sup>, E. R. Keim<sup>2</sup>, E. L. Woodbridge<sup>2</sup>, R. M. Stimpfle<sup>1</sup>, J. P. Koplow<sup>1</sup>, D. W. Kohn<sup>1</sup>, C. R. Webster<sup>3</sup>, R. D. May<sup>3</sup>, L. Pfister<sup>4</sup>, E. W. Gottlieb<sup>1</sup>, H. A. Michelsen<sup>1</sup>, G. K. Yue<sup>5</sup>, J. C. Wilson<sup>6</sup>, C. A. Brock<sup>6</sup>, H. H. Jonsson<sup>6</sup>, J. E. Dye<sup>7</sup>, D. Baumgardner<sup>7</sup>, M. H. Proffitt<sup>2</sup>, M. Loewenstein<sup>4</sup>, J. R. Podolske<sup>4</sup>, J. W. Elkins<sup>8</sup>, G. S. Dutton<sup>8</sup>, E. J. Hintsa<sup>1</sup>, A. E. Dessler<sup>9</sup>, E. M. Weinstock<sup>1</sup>, K. K. Kelly<sup>2</sup>, K. A. Boering<sup>1</sup>, B. C. Daube<sup>1</sup>, K. R. Chan<sup>4</sup>, S. W. Bowen<sup>4</sup>

**Abstract.** In situ measurements of hydrogen, nitrogen, and chlorine radicals obtained in the lower stratosphere during SPADE are compared to results from a photochemical model that assimilates measurements of radical precursors and environmental conditions. Models allowing for heterogeneous hydrolysis of N<sub>2</sub>O<sub>5</sub> agree well with measured concentrations of NO and ClO, but concentrations of HO<sub>2</sub> and OH are underestimated by 10 to 25%, concentrations of NO<sub>2</sub> are overestimated by 10 to 30%, and concentrations of HCl are overestimated by a factor of 2. Discrepancies for [OH] and [HO<sub>2</sub>] are reduced if we allow for higher yields of O(<sup>1</sup>D) from O<sub>3</sub> photolysis and for heterogeneous production of HNO<sub>2</sub>. The data suggest more efficient catalytic removal of O<sub>3</sub> by hydrogen and halogen radicals relative to nitrogen oxide radicals than predicted by models using recommended rates and cross sections. Increases in [O<sub>3</sub>] in the lower stratosphere may be larger in response to inputs of NO<sub>y</sub> from supersonic aircraft than estimated by current assessment models.

## Introduction

Data collected during the Stratospheric Photochemistry, Aerosols, and Dynamics Expedition (SPADE) in May 1993 offer a unique opportunity to investigate the chemistry of HO<sub>x</sub>, NO<sub>x</sub>, and ClO<sub>x</sub> radicals in the lower stratosphere. We assimilate into a photochemical model data for pressure, temperature, aerosol surface area, long-lived precursors of free radicals (O<sub>3</sub>, H<sub>2</sub>O, CH<sub>4</sub>, NO<sub>y</sub>, and Cl<sub>y</sub> inferred from CCl<sub>3</sub>F and CO<sub>2</sub>), total column ozone, and

planetary albedo obtained by the ER-2 aircraft on latitude transects from 15 to 58°N. Concentrations of radicals (OH, HO<sub>2</sub>, NO, NO<sub>2</sub>, ClO) and HCl are computed and compared to observations to test our understanding of key photochemical processes.

## Theory and Observation

We focus on segments of two flights, to Moffett Field, CA (37.4°N) from the south on 14 May 1993 (930514) and from the north on 18 May 1993 (930518), that provided the most complete set of measurements during SPADE. Each segment began with a descent from ~50 mb to ~120 mb near noon, followed by a climb and cruise at maximum altitude (~50 mb), and a second descent and ascent near the midpoint. Fig. 1 shows measurements (used as inputs to the photochemical model) of pressure, temperature, aerosol surface area, and long-lived radical precursors.

The aerosol surface area was measured by the Focused Cavity Aerosol Spectrometer (FCAS) and the Forward Scattering Spectrometer Probe (FSSP), optical particle counters that determine the size of ambient particles with diameters between 0.1 and 0.9 μm, and diameters between 0.4 and 20 μm, respectively. The surface area estimated by the FSSP for the overlap region between the two instruments was approximately 50% larger than the area measured by the FCAS. We have adopted an estimate of aerosol surface area for the size range 0.1 to 20 μm using data from the FCAS for the overlap region. Model results are relatively insensitive to this assumption, since total surface area changes by ~20% depending on which measurement is used for the overlap region.

Measurements of [NO<sub>y</sub>] were not available for the latter portion of 930514 and were estimated from data for [N<sub>2</sub>O] using the compact correlation observed between these species. Concentrations of inorganic chlorine (Cl<sub>y</sub>) were computed from in situ measurements of halogenated source gases and [CO<sub>2</sub>] [Woodbridge et al., 1994]. We adopted the mean of H<sub>2</sub>O concentrations reported by two instruments since the ~15% systematic difference between the measurements is not understood. Other inputs to the model include measured [CH<sub>4</sub>], [CO] estimated from its correlation with [O<sub>3</sub>] [Murphy et al., 1993], and [C<sub>2</sub>H<sub>6</sub>] and concentrations of inorganic Br estimated from their correlations with [N<sub>2</sub>O] [D. Blake, private communication, 1994; Schauffler et al., 1993].

Concentrations of HO<sub>x</sub> ([OH]+[HO<sub>2</sub>]) are sensitive to the column abundance of O<sub>3</sub> due to its role in regulating production of O(<sup>1</sup>D); partitioning of NO<sub>x</sub> ([NO]+[NO<sub>2</sub>]) is sensitive to planetary albedo due to photolysis of NO<sub>2</sub>. Photolysis rates were calculated

<sup>1</sup>Harvard University

<sup>2</sup>NOAA Aeronomy Laboratory

<sup>3</sup>Jet Propulsion Laboratory

<sup>4</sup>NASA Ames Research Center

<sup>5</sup>NASA Langley Research Center

<sup>6</sup>University of Denver

<sup>7</sup>National Center for Atmospheric Research

<sup>8</sup>NOAA Climate Monitoring and Diagnostics Laboratory

<sup>9</sup>Goddard Space Flight Center

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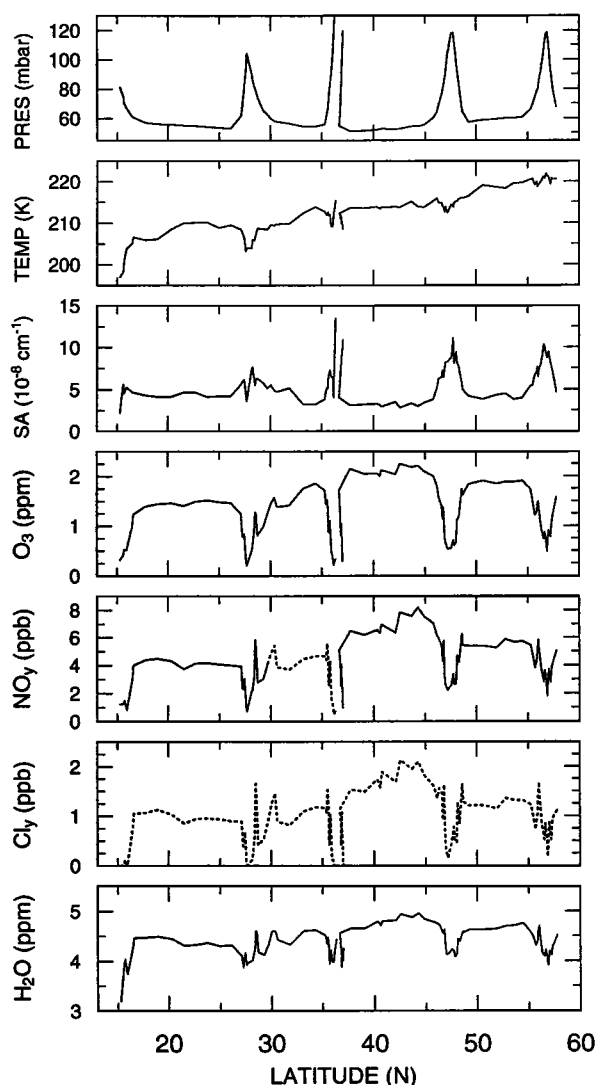


Figure 1. Values of pressure, temperature, aerosol surface area, and mixing ratios of  $O_3$ ,  $NO_y$ ,  $Cl_x$ , and  $H_2O$  obtained during the return segment of ER-2 flights 930514 and 930518. Dashed lines indicate values inferred from other tracers (see text).

using a radiative transfer model that accounts for Rayleigh and aerosol scattering [Prather, 1981] using ultraviolet albedo specified from observations by the Total Ozone Mapping Spectrometer (TOMS). Profiles for  $O_3$  were scaled to the column abundances measured by TOMS assuming changes occur only for altitudes  $< 24$  km (26 km for latitude  $> 50^\circ N$ ). Profiles for temperature and aerosol extinction for May 1993 were obtained from the National Meteorological Center and from observations by the Stratospheric Aerosol and Gas Experiment II, respectively.

The photochemical model includes 35 reactive species and approximately 220 chemical reactions. Reaction rates and absorption cross sections were adopted from DeMore et al. [1992], unless noted otherwise, except for extrapolations to longer wavelengths of cross sections for  $H_2O_2$ ,  $HNO_2$ , and  $HNO_4$ . A reaction probability of 0.1 was used for the heterogeneous hydrolysis of  $N_2O_5$  [DeMore et al., 1992]. The formulation of Hanson et al. [1994] was adopted for the rate of the heterogeneous hydrolysis of  $ClONO_2$ , which has a negligible effect on model results for temperatures encountered during these flights.

A Newton-Raphson iterative technique was used to find the set of diurnally varying species concentrations that repeats every 24

hours [Logan et al., 1978]; i.e., we assumed that each species reached a balance between production and loss, over 24 hours, for the temperature, pressure, and latitude at which an air parcel was sampled. Time constants for equilibration are  $< 1$  day for  $HO_x$ ,  $\sim 1$  week for  $NO_x$ , and  $\sim 1$  month for  $HCl$ . Winds were weak during May, the flow was primarily zonal, and the atmosphere does not have strong latitudinal gradients in the  $[ClONO_2]$  to  $[HCl]$  ratio; therefore, we expect on average relatively small deviations from steady state for  $[NO_x]$  and  $[ClONO_2]$ .

Model results appropriate for the solar zenith angle at the time of measurement are compared to observations in Fig. 2. Calculations neglecting heterogeneous chemistry underestimate concentrations of  $OH$ ,  $HO_2$ , and  $ClO$  and overestimate concentrations of

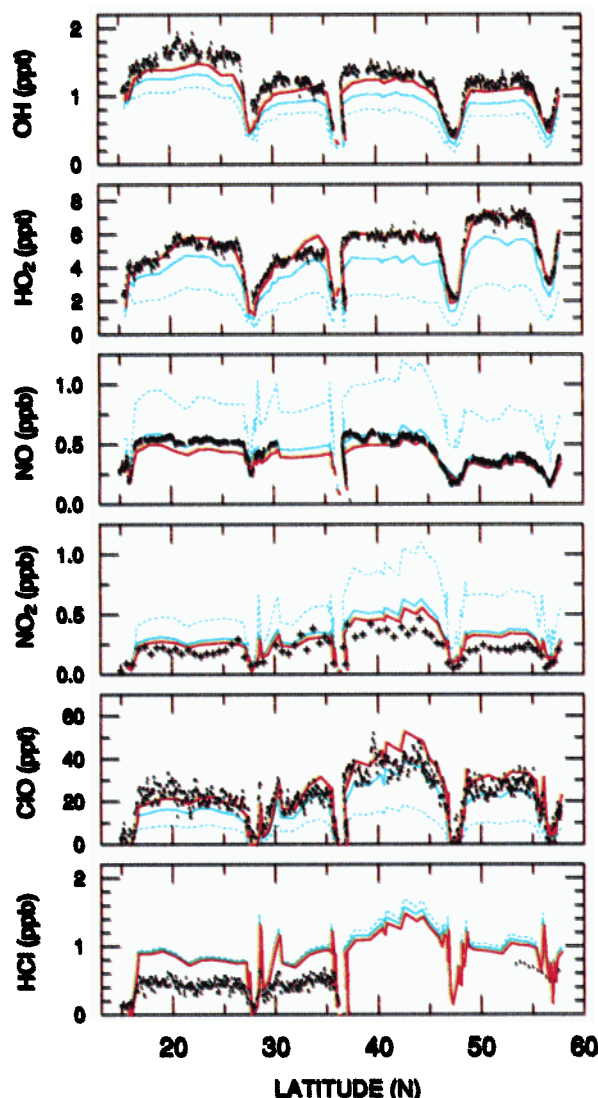


Figure 2. Measurements (points) of  $[OH]$ ,  $[HO_2]$ ,  $[NO]$ ,  $[NO_2]$ ,  $[ClO]$ , and  $[HCl]$  for 930514 and 930518 compared to model simulations using rates and cross sections from DeMore et al. [1992]: neglecting all heterogeneous processes (*JPL-Gas*, blue dotted line); including heterogeneous hydrolysis of  $N_2O_5$  and  $ClONO_2$  (*JPL-Het*, blue solid line); and same as *JPL-Het* except allowing for updated absorption cross sections for  $HNO_2$  and quantum yields of  $O(^1D)$ , and the heterogeneous production of  $HNO_2$  (*Model B*; red line). Measurements of  $[ClO]$  and  $[NO]$  (obtained every 16 and 1 seconds, respectively) have been smoothed using a 1 minute median filter.

NO and NO<sub>2</sub> by nearly a factor of 2, significantly larger than the uncertainty of measurement for each gas (2 $\sigma$  measurement uncertainties, including random and systematic effects, are estimated to be 30% for [OH], 40% for [HO<sub>2</sub>], 20% for [NO], 25% for [NO<sub>2</sub>], 25% for [ClO], and 20% for [HCl]).

Calculated concentrations of radicals are within the uncertainty of measurement for OH, HO<sub>2</sub>, NO, NO<sub>2</sub>, and ClO if we allow for heterogeneous hydrolysis of N<sub>2</sub>O<sub>5</sub> and ClONO<sub>2</sub> (*JPL-Het* in Fig. 2). Hence simultaneous observations of HO<sub>x</sub>, NO<sub>x</sub>, and ClO<sub>x</sub> radicals demonstrate the importance of heterogeneous reactions on sulfate aerosols (primarily hydrolysis of N<sub>2</sub>O<sub>5</sub>) in regulating the abundance of radicals in the lower stratosphere, consistent with previous studies using in situ measurements of [ClO] [King et al., 1991] and [NO] [Fahey et al., 1993].

Values of [OH] and [HO<sub>2</sub>] observed during early morning and late afternoon at 37°N are represented poorly by the *JPL-Het* model (discrepancies exceed a factor of 3 near sunrise) [Wennberg et al., 1994; Salawitch et al., 1994]. Concentrations of HO<sub>x</sub> during mid-day are underestimated by ~20%. Concentrations of NO<sub>2</sub> are overestimated by ~25% and [NO] is slightly underestimated, suggesting possible errors in the partitioning of NO<sub>x</sub> [Jaeglé et al., 1994]. Differences between observed and calculated concentrations of HO<sub>2</sub> and NO<sub>2</sub> during mid-day suggest contributions from HO<sub>x</sub> and halogen cycles to the removal rate of O<sub>3</sub> in the lower stratosphere are larger than predicted by models that use recommended rates and cross sections, although these differences lie within the 2 $\sigma$  uncertainty of the measurements.

Wennberg et al. [1994] proposed heterogeneous decomposition of HNO<sub>4</sub> as a source of HNO<sub>2</sub> to account for the rapid rise in [OH] and [HO<sub>2</sub>] at sunrise. This reaction would increase [HO<sub>x</sub>] at mid-day due to reduction of the OH+HNO<sub>4</sub> sink. Michelsen et al. [1994] suggested that photolysis of vibrationally and rotationally excited states of O<sub>3</sub> result in quantum yields for O(<sup>1</sup>D) approximately 25% higher than values recommended by DeMore et al. [1992], leading to enhanced production of HO<sub>x</sub> from the reaction of O(<sup>1</sup>D)+H<sub>2</sub>O. Recent measurements of the temperature-dependent absorption cross section for HNO<sub>3</sub> reported by Burkholder et al. [1993] result in a 20% reduction in the photolysis rate of HNO<sub>3</sub> for a temperature of 220 K compared to models using cross sections from DeMore et al. [1992], lowering calculated [NO<sub>x</sub>] and [HO<sub>x</sub>], and raising [ClO].

Agreement between theory and observation for [OH] and [HO<sub>2</sub>] is improved if we adopt absorption cross sections for HNO<sub>3</sub> from Burkholder et al. [1993] and quantum yields for O(<sup>1</sup>D) from Michelsen et al. [1994], and allow for the heterogeneous decomposition of HNO<sub>4</sub> to form HNO<sub>2</sub> with a reaction probability of 0.2 (*Model B*, Fig. 2). This model results in an excellent simulation of the diurnal variation of [OH] and [HO<sub>2</sub>] observed at 37°N [Salawitch et al., 1994].

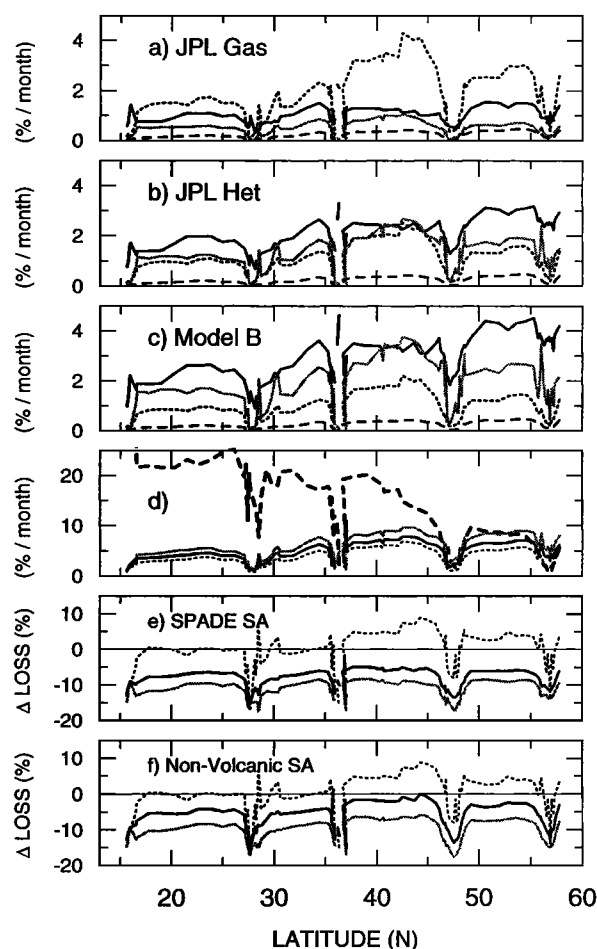
Comparisons between observed and calculated [NO<sub>x</sub>] and [ClO] are unable to distinguish between various heterogeneous models. Calculated values of [NO] and [NO<sub>2</sub>] are sensitive to uncertainties in the rates of processes that regulate the ratio of NO to NO<sub>2</sub> (including the photolysis rate of NO<sub>2</sub>) and the ratio of NO<sub>2</sub> to NO<sub>x</sub> (including aerosol surface area, the reaction probability of hydrolysis of N<sub>2</sub>O<sub>5</sub>, and the influence of variations in latitude of air parcels during the 2 weeks prior to measurement) [Kawa et al., 1993; R. Cohen et al., in preparation, 1994]. Comparisons between observed and calculated ClO are complicated further by uncertainties in estimating [Cl<sub>2</sub>] and processes that regulate production and loss of ClONO<sub>2</sub> and HCl. Stimpfle et al. [1994] demonstrate that in situ [ClO] and [NO<sub>2</sub>] are inversely correlated; therefore, errors in the simulation of NO<sub>x</sub> will be reflected directly in the simulation for ClO. Significant refinements in atmospheric

and laboratory observations are required to define the significance of the discrepancies for [NO<sub>x</sub>] and [ClO] illustrated in Fig. 2.

Concentrations of HCl computed using all models are higher than measured values by about a factor of 2. Our study demonstrates that this discrepancy does not arise from errors in simulating HO<sub>x</sub>. The origin of this discrepancy and its implications for understanding the response of O<sub>3</sub> in the lower stratosphere to natural and anthropogenic perturbations remain unclear.

### Effects of NO<sub>y</sub> Emitted from Aircraft on O<sub>3</sub>

The contributions of HO<sub>x</sub>, NO<sub>x</sub>, and halogen catalytic cycles to the loss rate of O<sub>3</sub> is shown in Fig. 3a-c. Models with hetero-



**Figure 3.** (a–c) The odd oxygen ([O]+[O<sub>3</sub>]) loss rate, averaged over 24 hours, for HO<sub>x</sub> (dark line; rate limiting step primarily HO<sub>2</sub>+O<sub>3</sub>), halogen (grey line; primarily BrO+ClO, ClO+HO<sub>2</sub>, BrO+HO<sub>2</sub>, and ClO+O), NO<sub>x</sub> (dotted line; primarily NO<sub>2</sub>+O), and O+O<sub>3</sub> (dashed line) catalytic cycles for the simulations shown in Fig. 2. (d) Total loss rate of odd oxygen, averaged over 24 hours, for the *JPL-Gas* (dotted line), *JPL-Het* (dark line), and *Model B* (grey line) simulations, and the production of odd oxygen from photolysis of O<sub>2</sub> (dashed line). (e) Change in the loss rate of odd oxygen (percent) calculated assuming a 20% increase in the concentration of NO<sub>y</sub> for the *JPL-Gas* (dotted line), *JPL-Het* (dark line), and *Model B* (grey line) simulations, using the observed aerosol surface area (Fig. 1). (f) Same as (e), except using estimates of aerosol surface area for background (non-volcanic) conditions ( $\sim 1 \times 10^{-8} \text{ cm}^{-1}$  at pressure = 60 mbar).

geneous chemistry on sulfate aerosols indicate larger contributions from  $\text{HO}_x$  and halogen cycles and larger total loss rates (Fig. 3d) than models based solely on gas phase reactions [Rodriguez et al., 1991; McElroy et al., 1992].

Emission scenarios for the proposed fleet of High Speed Civil Transports (HSCT) indicate possible increases in  $[\text{NO}_x]$  of 20 to 100% at ER-2 flight levels. The gas phase model predicts decreases in  $[\text{O}_3]$  as  $[\text{NO}_x]$  rises due to  $\text{NO}_x$ -related chemistry, in contrast to models with heterogeneous chemistry that predict increases due to deactivation of the more efficient  $\text{HO}_x$  and halogen cycles [Weisenstein et al., 1993]. The decrease in the chemical removal rate of  $\text{O}_3$  for an increase in  $[\text{NO}_x]$ , for aerosol loading encountered during SPADE, is ~30% larger for *Model B* than for *JPL-Het* (Fig. 3e), reflecting increased rates for  $\text{HO}_x$  and halogen cycles in *Model B*. Loss rates exhibit a more pronounced difference to a perturbation of  $[\text{NO}_x]$  for background (non-volcanic) aerosol loading due to larger contributions from the  $\text{NO}_x$  cycle in each heterogeneous model (Fig. 3f).

The region of the atmosphere accessible to the ER-2, 16 to 20 km, is characterized by slow rates for chemical removal of  $\text{O}_3$ . Perturbations to  $[\text{O}_3]$  at higher altitudes (20 to 30 km) by HSCT aircraft will be sensitive to chemical partitioning of radicals and to the transport of  $\text{NO}_x$  emitted from aircraft. Simultaneous measurements of  $\text{HO}_x$ ,  $\text{NO}_x$ , and  $\text{ClO}_x$  radicals and long-lived precursors at these altitudes are essential for constraining future assessment models.

## Conclusions

Models that include heterogeneous hydrolysis of  $\text{N}_2\text{O}_5$  on sulfate aerosols provide a good description of observed concentrations of hydrogen, nitrogen, and chlorine radicals in the lower stratosphere. Nevertheless, the relative contribution to chemical removal of  $\text{O}_3$  from cycles involving  $\text{HO}_x$  and halogens appears to be underestimated by models based on recommended rates and cross sections. Consequently, emission of  $\text{NO}_x$  from supersonic aircraft may result in larger increases in concentrations of  $\text{O}_3$  in the lower stratosphere than predicted by current assessment models [e.g., Weisenstein et al., 1993].

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R. J. Salawitch, Harvard University, Cambridge, MA 02138.

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